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(54) Method of recovering organic sulfur compound from liquid oil.

(57) The present relates to a method of recovering an organic sulfur compound useful from the viewpoint of industry from a liquid oil obtained from petroleum, oil sand, oil shale or coal. This recovery method comprises treating a liquid oil containing an organic sulfur compound with an oxidizing agent and separating the oxidized organic sulfur compound by separation means such as distillation, solvent extraction and/or adsorption means. The organic sulfur compound is recovered in the form of a sulfoxide compound and/or a sulfone compound.

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The present invention relates to a method of recovering organic sulfur compounds useful from the viewpoint of industry in the fields of production of medicines, agricultural chemicals, heat-resistant resins, etc., from mineral oils obtained from petroleum, oil sand, oil shale and coal, that is, liquid oils.

It is known from oil that liquid oils obtained from petroleum, oil sand, oil shale and coal contain various organic sulfur compounds. In recent years, for example, sulfur compounds contained in a fuel oil for diesel engines have attracted attention as one of the main culprits behind environmental pollution, and an urgent development of a usefuel desulfurization technique has been desired in the art. Thus, the organic sulfur compounds contained in mineral oils have been keenly regarded as a harmful substance, and the development of techniques aiming at removing the sulfur compounds has been made.

A technique for recovering an organic sulfur compound from an industrial gas, such as a waste gas, is disclosed in Japanese Patent Publication No. 26577/1978. In this method of recovering an organic sulfur compound from an industrial gas, a waste gas containing an organic sulfur compound is absorbed into a mineral oil under pressure to recover the organic sulfur compound as a high concentration gas. Specifically, the method of recovering an organic sulfur compound comprises depressurizing the mineral oil, absorbing the industrial gas containing an organic sulfur compound, diffusing the organic sulfur compound by steam, circulating the industrial gas through an absorption column for reuse and, at the same time, condensing a vapor mixture comprising the diffused organic sulfur compound, the mineral oil and steam to separate the mixture into an oily layer and a watery layer, and contacting the gas generated by the depressurization with the oily layer to provide a gas containing the organic sulfur compound in a high concentration. This method of recovering an organic sulfur compound, however, is silent on the recovery of an organic sulfur compound from a mineral oil.

U.S. Patent 3,341,448 by Ford discloses a method of oxidizing a sulfur compound contained in a hydrocarbon, which comprises oxidizing a sulfur compound contained in a hydrocarbon with an oxidizing agent and then thermally decomposing the resultant oxide in the presence of a catalyst in a hydrogen atmosphere at high temperature. In the Ford patent, the organic sulfur compound contained in a hydrocarbon is selectively oxidized and then decomposed at high temperature, so that the organic sulfur compound contained in a hydrocarbon is not recovered in such a state that the original chemical structure is maintained.

U.S. Patent 2,749,284 by Noble discloses a method which comprises oxidizing a sulfur compound contained in a hydrocarbon with an organic peroxide into an oxide such as a sulfoxide or a sulfone. The organic peroxide disclosed in the Noble patent is poor in the oxidizing capability and the specific reactivity to the organic sulfur compound (selectivity for the reaction with the organic sulfur compound). Therefore, it acts only on particular functional groups contained in a relatively small amount in the liquid oil, for example, thiol and dialkyl sulfides, and scarcely acts on chemically stable functional groups present in a large amount in gas oil and heavy fuel oil, such as benzothiophene and dibenzothiophene derivatives.

U.S. Patent 4,830,733 by Nagji describes the use of an adsorbent for removing a sulfur compound from a fluid. Although the Nagji patent is one relating to the recovery of a sulfur compound from a fluid with an adsorbent, it discloses, in essence, only the recovery of hydrogen sulfide from natural gas and does not relate to the adsorption of the oxidized fluid. Further, the substance adsorbed thereby is mainly hydrogen sulfide, and the use of a catalyst, maintenance, etc., are required of an apparatus for adsorbing the substance.

Since, however, the organic sulfur compound contained in a mineral oil is very similar to the mineral oil per se in the physical and chemical properties, general separation and purification means, such as distillation or solvent extraction, are not effective. A method of separating and removing an organic sulfur compound, which is mainly used for this purpose at the present time, comprises reacting a mineral oil with hydrogen gas under violent reaction conditions of a high temperature and a high pressure in the presence of a catalyst to convert the organic sulfur compound into harmful hydrogen sulfide and separating the hydrogen sulfide. Such a hydrogenating desulfurization method, however, cannot be applied when it is intended to isolate the organic sulfur compound from the mineral oil in such a state that the original chemical structure is maintained as much as possible to thereby utilizing the organic sulfur compound.

An aim of the present invention is to isolate an organic sulfur compound from a mineral oil in such a state that the original chemical structure thereof in the mineral oil, that is, liquid oil, is maintained as much as possible to thereby utilize the organic sulfur compound by providing a method which comprises oxidizing an organic sulfur compound with an oxidizing agent and recovering the oxidized organic sulfur compound from the system by separation means, such as distillation, in a simple and economical manner.

The present invention relates to a method of recovering an organic sulfur compound from a liquid oil, which comprises treating a liquid oil containing an organic sulfur compound obtained from petroleum, oil sand, oil shale or coal with an oxidizing agent, separating the oxidized sulfur compound by distillation, solvent extraction and/or adsorption means to isolate the oxidized organic sulfur compound from the liquid oil. In this recovery method, the organic sulfur compound recovered is preferably a sulfoxide compound and/or a sulfone compound.

More preferably, the present invention relates to a method of recovering an organic sulfur compound from a liquid oil, comprising the steps of:

treating the liquid oil at -20 to 140 °C with an oxidizing agent selected from among an oxygen gas, air, an ozone gas, a chlorine gas, hydrogen peroxide, peracetic acid, performic acid, a mixture of hydrogen peroxide water with formic acid, perbenzoic acid, a mixture of hydrogen peroxide water with benzoic acid, perchloroacetic acid, a mixture of hydrogen peroxide water with chloroacetic acid, perdichloroacetic acid, a mixture of hydrogen peroxide water with dichloroacetic acid, pertrichloroacetic acid, a mixture of hydrogen peroxide water with trichloroacetic acid, pertrifluoroacetic acid, a mixture of hydrogen peroxide water with trifluoroacetic acid, permethanesulfonic acid, a mixture of hydrogen peroxide water with methanesulfonic acid, hypochlorous acid, and an aqueous hypochlorite solution,

oxidizing the organic sulfur compound contained in the liquid oil to thereby raise the boiling point and melting point of the organic sulfur compound and convert into an oxidized organic sulfur compound with a different solubility based on the polarity of the molecule, and

applying the system to a recovery treatment selected from among distillation, solvent extraction, low-temperature separation, adsorbent treatment and separation by washing to separate and remove the oxidized organic sulfur compound from the liquid oil through the utilization of differences in the boiling point, melting point and/or solubility between the organic sulfur compound and the oxidized organic sulfur compound.

In this recovery method, the liquid oil is preferably selected from among naphtha (b.p.: up to 30°C), gasoline (b.p.: 30 - 220 °C), kerosine (b.p.: 220 - 300 °C), gas oil (b.p.: 300 - 360 °C) and heavy fuel oil.

An embodiment of the present invention comprises reacting the liquid oil with a peracid oxidizing agent or a hypochlorous acid oxidizing agent at a temperature in the range of from 0 to 140 °C while agitating, separating an oily phase from the reaction mixture after the reaction, adding an aqueous alkali solution to the oil to wash the same, further washing the oil with water, and recovering the resultant oxidized organic sulfur compound.

Another embodiment of the present invention comprises reacting the liquid oil with a gaseous oxidizing agent at a temperature in the range of -20 to 50 °C while bubbling the gaseous oxidizing agent, adding a reducing agent to the reaction mixture for washing the oil, further washing the oil with water, and recovering the resultant oxidized organic sulfur compound from the oil.

A further embodiment of the present invention comprises reacting the liquid oil with a gaseous oxidizing agent at a temperature in the range of -20 to 50 °C in the presence of a photosensitizer in such a manner that the gaseous oxidizing agent is bubbled while irradiating the reaction system with light, adding a reducing agent to the reaction mixture for washing the oil, further washing the oil with water, and recovering the resultant oxidized organic sulfur compound.

A further embodiment of the present invention comprises treating the liquid oil with an oxidizing agent and distilling the treated liquid oil in the boiling point range of the liquid oil before the treatment in a rectifier to recover the oxidized organic sulfur compound as a distillation residue.

A further, embodiment of the present invention comprises treating the liquid oil with an oxidizing agent, distilling the treated liquid oil in the boiling point range of the liquid oil before the treatment in a rectifier, and passing the distillate through a column packed with an adsorbent selected from among activated carbon, silica gel, alumina, and combinations of two or more of them to adsorb the oxidized organic sulfur compound on the adsorbent.

A further embodiment of the present invention comprises treating the liquid oil with an oxidizing agent, cooling the treated liquid oil to a temperature at which insoluble components deposit, allowing the oil to stand as such, separating an oily component from the system by means of a filter or a separator and distilling the oil in the boiling point range of the liquid oil before the treatment in a rectifier to recover the oxidized organic sulfur compound as a low-temperature insoluble and a distillation residue.

A further embodiment of the present invention comprises treating the liquid oil with an oxidizing agent, cooling the treated liquid oil to a temperature at which insoluble components deposit, allowing the oil to stand as such, separating an oily component from the system by means of a filter or a separator, distilling the oil in the boiling point range of the liquid oil before the treatment in a rectifier, and passing the distillate through a column packed with an adsorbent selected from among activated carbon, silica gel, alumina, and combinations of two or more of them to recover the oxidized organic sulfur compound remaining in the distillate.

In the present invention, the organic sulfur compound contained in the liquid oil is preferably a thiophene compound which has a divalent sulfur atom and is chemically stable. The divalent sulfur atom of the thiophene compound is combined with oxygen by an oxidation reaction to convert the compound into a sulfoxide, a sulfone or a sulfonic acid containing a sulfur atom having a higher valency, and the formed sulfoxide, sulfone or sulfonic acid is recovered.

In summary, the recovery method of the present invention comprises pretreating a liquid oil, that is, a mineral oil with various oxidizing agents to convert an organic sulfur compound into an oxide with the original mo-

lecular skeleton thereof substantially maintained as such, and recovering the oxidized organic sulfur compound useful from the viewpoint of industry from the mineral oil in an efficient and simple manner at a low cost through the utilization of an accompanying change in the physical and chemical properties, such as the polarity, boiling point and melting point of the molecule.

In the present invention, at the outset, an organic sulfur compound having a divalent sulfur atom and contained in a mineral oil is reacted with various oxidizing agents different from each other in the oxidizing capability to convert the organic sulfur compound into a sulfoxide compound and a sulfone compound successively and the reaction product is separated from other components and recovered through the utilization of a change in the physical and chemical properties of the reaction product caused by the chemical conversion. For example, the oxidized organic sulfur compound can be easily separated and recovered by distillation through the utilization of the fact that the boiling point of the oxidized organic sulfur compound is much higher than that of the organic sulfur compound in a nonoxidized state. Further, the oxidized organic sulfur compound can be selectively extracted and recovered through the utilization of a change in the solubility in various solvents based on an increase in the polarity of the molecule.

Further, since the change in the chemical properties remarkably improves also the adsorbability to adsorbents, such as silica gel or alumina, the adsorption, separation and purification with the use of an adosrbent can be easily conducted at a very high efficiency. Further, a combination of the above-described separation and recovery methods can provide more favorable results.

Further, the method of recovering an organic sulfur compound according to the present invention enables only a particular group of organic sulfur compounds to be selectively isolated by conducting reactions while properly selecting the oxidizing agents through the utilization of the difference in the reactivity among the organic sulfur compounds per se in the mineral oil in the oxidation reaction. Specifically, when use is made of an oxidizing agent capable of selectively oxidizing an organic sulfur compound containing a divalent sulfur atom into a sulfoxide compound alone, the oxidized organic sulfur compound can be isolated as a sulfoxide. Further, when use is made of an oxidizing agent having a capability of oxidizing the organic sulfur compound into a sulfone compound, the oxidized organic sulfur compound can be isolated as a sulfone. The utilization of such a property that the reactivity remarkably changes according to the steric hindrance based on the change in the structure of the organic sulfur compound molecule enables a group of particular organic sulfur compounds having such a steric hindrance to be selectively isolated by properly selecting the reactivity of the oxidizing agents.

Further, in the method of recovering an organic sulfur compound according to the present invention, the mineral oil containing an organic sulfur compound is selected from among crude oil, oil shale, oil sand, coal tar, liquefied oil of coal, petroleum products obtained directly therefrom, that is, naphtha, gasoline, kerosine, gas oil, heavy fuel oil, pitch and indirect petroleum products obtained by chemical decomposition of the above-described mineral oils.

Examples of the oxidizing agent which may be used in the method of recovering an organic sulfur compound according to the present invention include oxygen gas, air, nitrogen tetraoxide gas, ozone gas, chlorine gas, bromine, sodium metaperiodate, potassium bichromate, potassium permanganate, anhydrous chromic acid, hypochlorous acid, hydrogen peroxide, peracetic acid, a mixture of hydrogen peroxide water with acetic acid, performic acid, a mixture of hydrogen peroxide water with formic acid, m-chloroperbenzoic acid, a mixture of hydrogen peroxide water with m-chlorobenzoic acid, perchloroacetic acid, a mixture of hydrogen peroxide water with chloroacetic acid, perdichloroacetic acid, a mixture of hydrogen peroxide water with dichloroacetic acid, pertrichloroacetic acid, a mixture of hydrogen peroxide water with trichloroacetic acid, pertrifluoroacetic acid, a mixture of hydrogen peroxide water with trifluoroacetic acid, permethanesulfonic acid, a mixture of hydrogen peroxide water with methanesulfonic acid, persulfuric acid, and a mixture of hydrogen peroxide water with sulfuric acid.

The method of recovering an organic sulfur compound according to the present invention comprises reacting a mineral oil with an organic peracid oxidizing agent or an inorganic oxidizing agent at a temperature in the range of from 0 to 100 °C with stirring, separating an oil component after the completion of the reaction, adding water to the oil component to wash the same, and recovering the resultant oxidized organic sulfur compound from the liquid oil.

Another embodiment of the method of recovering an organic sulfur compound according to the present invention comprises treating a liquid oil with an oxidizing agent and then with an extractant selected from among acetonitrile, propionitrile, butyronitrile, nitromethane, nitroethane, nitropropane, nitrobenzene, dimethyl sulfoxide, N,N'-dimethylformamide, N,N'-dimethylacetamide, N-methylpyrrolidinone, trimethyl phosphate, triethyl phosphate, hexamethylphosphoric amide, phosphorane, and mixtures thereof with water in a concentration of from 0 to 50 % to recover the resultant oxidized organic sulfur compound from the liquid oil.

Physical and chemical changes (solubility based on the polarity of the molecule) of the organic sulfur com-

pound formed by the oxidation reaction are important to the solvent extraction of the sulfoxide, sulfone, sulfonic acid, etc., formed by the oxidatoin of the organic sulfur compound present in the liquid oil. With respect to oxidatoin products of benzothiophene and dibenzothiophene present in a large amount particularly in gas oil and heavy fuel oil, aprotic dipolar solvents, such as acetone and dimethylformamide (DMF), have much higher partition coefficients than those of alcohols such as methanol. Thus, the extraction of the oxidized organic sulfur compound contained in the liquid oil with the organic solvent exhibits the intended effect only when various sulfur compounds contained in the liquid oil can be oxidized at a good efficiency in a high yield.

A further embodiment of the method of recovering an organic sulfur compound according to the present invention comprises treating the liquid oil with an oxidizing agent, passing the treated liquid oil through an adsorption column packed with an adsorbent selected from among activated clay, silica gel, alumina, and mixtures thereof to adsorb the formed organic sulfur oxide on the activated clay, and desorbing and separating the adsorbed organic sulfur oxide with a solvent selected from among methanol, ethanol, propanol, butanol, acetone, acetonitrile, nitromethane, and mixtures thereof to recover the oxidized organic sulfur compound from the liquid oil.

A still further embodiment of the method of recovering an organic sulfur compound according to the present invention comprises reacting a liquid oil fractoin obtained by distillation in the boiling point range as narrow as possible in a rectifying column with an oxidizing agent, separating an oil component, washing the oil component with water, and redistilling the oil component in the same boiling point range as that in the distillation of the liquid oil before the treatment with the oxidizing agent to concentrate and recover the resultant oxidized organic sulfur compound in the distillation residue.

EXAMPLES:

The method of recovering an organic sulfur compound according to the present invention will now be described with reference to the following non-limiting Examples.

EXAMPLE 1

100 ml of a gas oil (b.p. range: 300 - 360 °C; combustible sulfur content: 0.53 % by weight) was cooled to 0 °C in a 200-ml hard glass round-bottomed flask equipped with a homogenizer agitator, a reflux condenser and a gas blow tube and agitated for one hour while passing air containing ozone (about 1.0 %) into the gas oil. After the supply of ozone was stopped, only air was further passed into the gas oil for additional one hour, and agitation was continued for additional one hour while gradually raising the temperature of the flask to 20 °C. 50 ml of a 2 N aqueous sodium sulfite solution was added to the reaction mixture to wash the same. After the reaction mixture was further washed with water, the gas oil layer and the tar layer were separated from each other. The gas oil layer was distilled in a rectifier to provide 92 ml of a fraction having a boiling point in the range of from 300 to 360 °C and 8 ml of a distillation residue. The distillation fraction had a sulfur content of 0.32 % and was mainly composed of benzothiophene and dibenzothiophene derivatives. The recovery of the organic sulfur compound in the distillation residue and the tar was 72 % in terms of sulfur, and the oxidation product was mainly composed of a sulfone compound.

EXAMPLE 2

100 ml of a gas oil (b.p. range: 300 - 360 °C; combustible sulfur content: 0.53 % by weight) was put in a 200-ml hard glass round-bottomed flask equipped with a homogenizer agitator and a reflux condenser and 10 ml of hydrogen peroxide water (30 %) and 10 ml of formic acid were added thereto. After the mixture was stirred at 20 °C for one hour, the reaction temperature was raised to 50 °C, and stirring was continued for additional one hour. After the completion of the reaction, the reaction mixture was cooled to 0 °C and allowed to stand to separate tar and a gas oil layer followed by washing with a 2 N aqueous sodium sulfite solution and further with water. The gas oil layer was distilled in a rectifier to provide 86 ml of a fraction having a boiling point in the range of from 300 to 360 °C and 12 ml of a distillation residue. The distillation fraction had a sulfur content of 0.04 % and was mainly composed of benzothiophene and dibenzothiophene derivatives. The recovery of the organic sulfur compound in the distillation residue and the tar was 97 % in terms of sulfur, and the oxidation product was mainly composed of a sulfone compound.

EXAMPLE 3

100 ml of a gas oil (b.p. range: 300 - 360 °C; combustible sulfur content: 0.53 % by weight) was put in a

200-ml hard glass round-bottomed flask equipped with a homogenizer agitator and a reflux condenser and 10 ml of hydrogen peroxide water (30 %) and 10 ml of dichloroacetic acid were added thereto. After the mixture was stirred at 40 °C for one hour, the reaction temperature was raised to 70 °C, and stirring was continued for additional one hour. After the completion of the reaction, the reaction mixture was cooled to 0 °C and allowed to stand to separate tar and a gas oil layer followed by washing with a 2 N aqueous sodium sulfite solution and further with water. The gas oil layer was again separated, and 10 ml of nitromethane was added thereto. The mixture was vigorously stirred for one hour and allowed to stand, and the gas oil layer and the nitromethane layer were separated from each other. 96 ml of the resultant gas oil layer had a sulfur content of 0.03 % and was mainly composed of benzothiophene and dibenzothiophene derivatives. The recovery of the organic sulfur compound in the nitromethane solution and the tar was 97 % in terms of sulfur, and the oxidation product was mainly composed of a sulfone compound.

EXAMPLE 4

100 ml of a heavy fuel oil (combustible sulfur content: 1.87 % by weight) was put in a 200-ml hard glass round-bottomed flask equipped with a homogenizer agitator and a reflux condenser and 10 ml of hydrogen peroxide water (30 %) and 10 ml of formic acid were added thereto. After the mixture was stirred at 30 °C for one hour, the reaction temperature was raised to 50 °C, and stirring was continued for additional one hour. After the completion of the reaction, the upper layer of the reaction mixture separated into two layers was separated by means of a separatory funnel and washed with a 2 N aqueous sodium sulfite solution and further with water. The heavy fuel oil layer was again separated and 50 ml of an aqueous N,N'-dimethylformamide solution containing 10 % of water was added thereto. The mixture was vigorously stirred at room temperature for one hour and allowed to stand, and the heavy fuel oil layer and the N,N'-dimethylformamide layer containing 10 % of water were separated from each other. 93 ml of the resultant heavy fuel oil layer had a sulfur content of 0.21 % and was mainly composed of benzothiophene and dibenzothiophene derivatives. The recovery of the organic sulfur compound in the N,N'-dimethylformamide solution and the tar was 89 % in terms of sulfur, and the oxidation product was mainly composed of a sulfone compound.

EXAMPLE 5

100 ml of a heavy fuel oil (combustible sulfur content: 1.87 % by weight) and 20 ml of distilled water were put in a 200-ml hard glass round-bottomed flask equipped with a homogenizer agitator, a reflux condenser and a gas blow tube, and a reaction was allowed to proceed while bubbling a chlorine gas at 0 °C for one hour. After the completion of the reaction, the heavy fuel oil layer was separated by means of a separatory funnel and washed with a 2 N aqueous sodium sulfite solution and further with distilled water. The heavy fuel oil layer was again separated and 5 ml of trimethyl phosphate containing 10 % of water was added thereto. The mixture was vigorously stirred at room temperature for 2 hours and then allowed to stand to separate the mixture into a mineral layer and a layer of trimethyl phosphate containing 10 % of water. 92 ml of the resultant heavy fuel oil layer had a sulfur content of 0.35 % and was mainly composed of benzothiophene and dibenzothiophene derivatives. The recovery of the organic sulfur compound in the trimethyl phasophate solution was 83 % in terms of sulfur, and the oxidation product thereof was mainly composed of a sulfoxide compound.

EXAMPLE 6

50 g of coal tar (combustible sulfur content: 0.67 % by weight) and 10 ml of benzene as a viscosity depressant were put in a 200-ml hard glass round-bottomed flask equipped with a homogenizer agitator and a reflux condenser and 5 ml of hydrogen peroxide water (30 %) and 10 ml of formic acid were added thereto to conduct a reaction at 40 °C for 3 hours. After the completion of the reaction, the coal tar layer was separated and washed with a 2 N aqueous sodium sulfite solution, and the coal tar layer was again separated. 100 ml of an N-methylpyrrolidinone solution containing 10 % of water was added thereto, and the mixture was vigorously stirred at room temperature for one hour and then allowed to stand to separate the mixture into a coal tar layer and an N-methylpyrrolidinone layer. The recovery of the organic sulfur compound in the N-methylpyrrolidinone solution was 79 % in terms of sulfur, and the oxidation product was mainly composed of sulfone compounds of benzothiophene and dibenzothiophene derivatives.

EXAMPLE 7

100 ml of a gas oil (b.p. range: 300 - 360 °C; combustible sulfur content: 0.53 % by weight) was put in a

200-ml hard glass round-bottomed flask equipped with a homogenizer agitator and a reflux condenser and 10 ml of hydrogen peroxide water (30 %) and 10 ml of formic acid were added thereto. After the mixture was vigorously stirred at 20 °C for one hour, the reaction temperature was raised to 50 °C, and stirring was continued for additional one hour. After the completion of the reaction, the reaction mixture was cooled to 0 °C and allowed to stand to separate tar and a gas oil layer followed by washing with water. 95 ml of the gas oil layer was passed through a column packed with an adsorbent comprising a mixture of 2.5 g of alumina with 2.5 g of silica gel. The material adsorbed on the adsorbent was eluted with 100 ml of acetone and recovered. The sulfur content of the resultant acetone solution was 0.51 %. In other words, the recovery of the organic sulfur compounds was 96 % in terms of sulfur, and the oxidation product was mainly composed of sulfone compounds of benzothiophene and dibenzothiophene derivatives.

EXAMPLE-8

A series of experiments were made to react various organic sulfur compounds with formic acid/hydrogenperoxide (30%) oxidation system. In a typical experiment, 10ml of formic acid and 10ml of hydrogenperoxide(30%) were mixed, and then 100ml of cyclohexane solution contained 0.02mole of organic sulfur compound was added. The mixture was vigorously stirred for one hour at 20 °C, and then the reaction temperature was raised to 50 °C and the stirring was continued for one more hour. Separation of the cyclohexane layer was followed by washing with fresh water and drying over anhydrous $MgSO_4$, and it was analyzed by gas chromatography, infrared and magnetic resonance spectrometried. Results of these experiments are shown in Table 1.

TABLE 1

	Product (%)		
Sulfur Compound	Sulfoxide	Sulfone	Unreacted
Dibenzothiophene	0	98	0
Benzothiophene	0	87	0
Diphenylsulfide	0	99	0
Di-n-butylsulfide	0	98	0
Methylphenylsulfide	0	97	0

EXAMPLE-9

Commercial diesel fuel(sulfur content; 0.53%) were treated with several oxidants and the organic sulfur components were separated by the N,N'-dimethylformamide (DMF)-extraction and the silica-gel absorption.

A typical example was as follows: To 100ml of diesel fuel 0.2 moles of t-butylhydroperoxide was added, and the mixture was vigorously stirred for one hour at room temperature and then one more hours at 80 °C. After the reaction, the mixture was washed with aqueous Na_2SO_3 solution and fresh water. The separated diesel fuel layer was dried over anhydrous $MgSO_4$. The organic sulfur components in the resulted diesel fuel was separated by the DMF-extraction and the silica-gel column chromatography. Results of these experiments are shown in Table 2.

TABLE 2

Oxidant	Sulfur content in fuel(%) after DMF-extracted [a]	after SiO_2-absorbed [b]
None	0.46	0.44
t-butylhydroperoxide	0.41	0.42
$KMnO_4$/water(30%)	0.23	0.18
formic acid/H_2O_2 (30%)	0.02	< 0.01 [c]

a) Volume ratio of DMF/fuel was 1/1, shaked at room temperature 30 minutes.

b) Weight ratio of SiO_2/fuel was 1/20.

c) Yield of recovered sulfur component with dichloromethane eluent was almost quantitative based on sulfur analyses.

Claims

1. A method of recovering an organic sulfur compound from a liquid oil, which comprises treating a liquid oil containing an organic sulfur compound obtained from petroleum, oil sand, oil shale or coal with an oxidizing agent, separating the oxidized organic sulfur compound by distillation, solvent extraction and/or adsorption means to isolate the oxidized organic sulfur compound from said liquid oil.

2. A method of recovering an organic sulfur compound from a liquid oil according to claim 1, wherein the organic sulfur compound recovered is a sulfoxide compound and/or a sulfone compound.

3. A method of recovering an organic sulfur compound from a liquid oil according to claim 1, comprising the steps of:

   treating said liquid oil at -20 to 140 °C with an oxidizing agent selected from among an oxygen gas, air, an ozone gas, a chlorine gas, hydrogen peroxide, peracetic acid, a mixture of hydrogen peroxide water with an acid, performic acid, a mixture of hydrogen peroxide water with formic acid, perbenzoic acid, a mixture of hydrogen peroxide water with benzoic acid, perchloroacetic acid, a mixture of hydrogen peroxide water with chloroacetic acid, perdichloroacetic acid, a mixture of hydrogen peroxide water with dichloroacetic acid, pertrichloroacetic acid, a mixture of hydrogen peroxide water with trichloroacetic acid, pertrifluoroacetic acid, a mixture of hydrogen peroxide water with trifluoroacetic acid, permethanesulfonic acid, a mixture of hydrogen peroxide water with methanesulfonic acid, hypochlorous acid and an aqueous hypochlorite solution,

   oxidizing the organic sulfur compound contained in the liquid oil to thereby raise the boiling point and melting point oi the organic sulfur compound and convert into an oxidized organic sulfur compound with a different solubility based on the polarity of the molecule, and

applying the system to a recovery treatment selected from among distillation, solvent extraction, low-temperature separation, adsorbent treatment and separation by washing to separate and remove the oxidized organic sulfur compound from the liquid oil through the utilization of differences in the boiling point, melting point and/or solubility between the organic sulfur compound and the oxidized organic sulfur compound.

4. A method of recovering an organic sulfur compound from a liquid oil according to claim 1, wherein the liquid oil is selected from among naphtha (b.p.: up to 30 °C), gasoline (b.p.: 30 - 220 °C), kerosine (b.p.: 220 - 300 °C), gas oil (b.p.: 300 - 360 °C) and heavy fuel oil.

5. A method of recovering an organic sulfur compound from a liquid oil according to claim 1, which comprises reacting said liquid oil with a peracid oxidizing agent or a hypochlorous acid oxidizing agent at a temperature in the range of from 0 to 140 °C while agitating, separating an oily phase from the reaction mixture after the reaction, adding an aqueous alkali solution to the oil to wash the same, further washing the oil with water, and recovering the resultant oxidized organic sulfur compound.

6. A method of recovering an organic sulfur compound from a liquid oil according to claim 1, which comprises reacting said liquid oil with a gaseous oxidizing agent at a temperature in the range of -20 to 50 °C while bubbling the gaseous oxidizing agent, adding a reducing agent to the reaction mixture for washing the oil, further washing the oil with water, and recovering the the resultant oxidized organic sulfur compound from the oil.

7. method of recovering an organic sulfur compound from a liquid oil according to claim 1, which comprises reacting said liquid oil with a gaseous oxidizing agent at a temperature in the range of from -20 to 50 °C in the presence of a photosensitizer in such a manner that the gaseous oxidizing agent is bubbled while irradiating the reaction system with light, adding a reducing agent to the reaction mixture for washing, the oil, further washing the oil with water, and recovering the resultant oxidized organic sulfur compound.

8. A method of recovering an organic sulfur compound from a liquid oil according to claim 1, which comprises treating the liquid oil with an oxidizing agent and distilling the treated liquid oil in the boiling point range of the liquid oil before the treatment in a rectifier, to recover the oxidized organic sulfur compound as a distillation residue.

9. A method of recovering an organic sulfur compound from a liquid oil according to claim 1, which comprises treating the liquid oil with an oxidizing agent, distilling the treated liquid oil in the boiling point range of the liquid oil before the treatment in a rectifier, and passing the distillate through a column packed with an adsorbent selected from among activated carbon, silica gel, alumina, and combinations of two or more of them to adsorb the oxidized organic sulfur compound on the adsorbent.

10. A method of recovering an organic sulfur compound from a liquid oil according to claim 1, which comprises treating the liquid oil with an oxidizing agent, cooling the treated liquid oil to a tempearture at which insoluble components deposit, allowing the oil to stand as such, separating an oily component from the system by means of a filter or a separator, and distilling the oil in the boiling point range of the liquid oil before the treatment in a rectifier to recover the oxidized organic sulfur compound as a low-temperature insoluble and a distillation residue.

11. A method of recovering an organic sulfur compound from a liquid oil according to claim 1, which comprises treating the liquid oil with an oxidizing agent, cooling the treated liquid oil to a temperature at which insoluble components deposit, allowing the oil to stand as such, separating an oily component from the system by means of a filter or a separator, distilling the oil in the boiling point range of the liquid oil before the treatment in a rectifier, and passing the distillate through a column packed with an adsorbent selected from among activated carbon, silica gel, alumina, and combinations of two or more of them to recover the oxidized organic sulfur compound remaining in the distillate.

12. A method of recovering an organic sulfur compound from a liquid oil according to claim 1, wherein the organic sulfur compound contained in said liquid oil is a thiophene compound which has a divalent sulfur atom and is chemically stable, and the divalent sulfur atom of the thiophene compound is combined with oxygen by an oxidation reaction to convert the compound into a sulfoxide, a sulfone or a sulfonic acid containing a sulfur atom having a higher valency.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 30 2642

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-3 551 328 (TEXACO) * claims 1,3 * * example 1 *	1,3,4,6,8	C10G53/14
A	FR-A-1 472 280 (ESSO) * claims 1,2,3 *	1,2,3,5,12	
D,A	US-A-2 749 284 (BP) * claims 1,2,3,4,5,6 *	1,3,4,8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C10G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 JUNE 1993	Oswald De Herdt

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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E : earlier patent document, but published on, or after the filing date
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